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MINERAL ZIRCON: A NOVEL THERMOLUMINESCENCE GEOCHRONOMETER

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Mineral zircon contains trace amounts (typically 10–1000ppm) of the α -emitters uranium and thorium, which irradiate this mineral internally. This outstanding feature of zircon turns out to be extremely useful when this mineral is applied as a thermoluminescence (TL) dating medium, because the build-up of the age-dependent luminescence is dominated by the presence of well-defined internal radioactive sources and the contributions to the dose from external radiation sources are two orders of magnitude smaller. The results presented in this paper have led us to the conclusion that for zircon dating it is necessary to carefully select the best and homogeneous zircon grains of the highest optical quality. For successful dating experiments on very young and historically well-defined coastal dune sands, selection of the most stable luminescence component by means of narrow band interference filters is needed. Our results suggest that ultimately optical zircon dating will allow us to determine the age of extremely young samples (*e.g.* 12 months!).

Keywords: Zircon; Thermoluminescence; Geochronological dosimetry; Dating

1. INTRODUCTION

The generation of TL by exposure of minerals (in particular quartz) to radiation sources forms the basis for geochronometers, measuring the time elapsed since burial of sediment by more recent layers. Since the early 1970's [1–6] several investigators have recognized that zircon is, in principle, an excellent mineral for TL geochronometry, especially for samples from the Quaternary. Although the Quaternary is the shortest geological period (0.04% of the geological time) it is the most studied one, by far. Thus, the interest in Quaternary geochronology is high, and is not restricted to geological specialists, because high-resolution histories of Quaternary events are important issues in *e.g.* Global Change studies, paleo-climate research and archaeology. Possibly, the zircon TL geochronometer could partly fill the gap between the dating range provided by the radiocarbon method and those of other dating tools, such as K/Ar.

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Thus far for several reasons the attempts to apply zircon for TL dating have been unsuccessful and unfortunately, efforts to develop this promising dating method have been abandoned by more and more scientists. At the same time the development of improved technologies and the impressive results of quartz TL and Optically Stimulated Luminescence (OSL) dating [7–10] have boosted the attention for quartz dating methods.

TL in mineral zircon is predominantly due to the presence of trace amounts of uranium and thorium and not to external radiation sources that cannot be measured reliably. The chief obstacles to the successful development of zircon luminescence dating have been the fading of laboratory-irradiated zircon, optical (and possibly chemical) inhomogeneities and zoning of mineral zircon [11–14]. For reliable dating experiments on sediment samples one should (i) select the most homogeneous zircon grains of the highest optical quality and (ii) solve (or at least drastically reduce) the problems of fading by selecting the most stable component of the TL spectrum for the dating experiment.

Thermoluminescence of minerals originates from lattice defect centres created by natural radioactivity. Important defect centres in irradiated zircon are several SiO_m^{n-} electron or hole excess centres (with electronic properties that depend on the values of m and n) and a variety of rare earth ions (with valences 3+ or 4+, depending on whether or not the ion trapped a radiation-induced hole). For dating one needs a well-defined calibration mechanism to set the time $t=0$. This can be achieved in nature, because under favourable conditions exposure of mineral zircon to full sunlight completely destroys the centres producing the TL signal. Therefore the dating “clock” is started after the last exposure to sunlight (optical resetting), *i.e.* the TL intensity is a measure of the irradiation dose accumulated since last deposition.

Most zircon crystals contain trace amounts of uranium and thorium, which irradiate the mineral internally at dose rates much higher than those from external sources, such as cosmic rays and β or γ -irradiation from *e.g.* 40 K in distant *K*-feldspar grains. Detrital zircon in sedimentary deposits varies in colour from transparent and colourless to pink, blue, violet, very dark and even completely black. As a result, the luminescence properties and the TL efficiency reveal enormous variations as well. Although the crystal structure of zircon is stable and quite resistant to ionising radiation, it is often damaged very heavily by the extremely high total natural doses of α -particles ($>10^9$ Gy), because of the in many cases enormous ages of zircon crystal lattice (which can be between several hundred million years to several billion years). As a result of these extremely high doses zircon might be transformed to a disordered or *metamict* state. It is clear that heavily damaged grains will not have favourable optical and resetting properties and to our knowledge there is no information showing that metamict grains re-crystallise during exposure to (sun)light. On the other hand thermal resetting of heavily damaged grains might be possible, implying that heavily damaged zircon grains in pottery could eventually be used for dating after firing at high temperatures.

Efforts to develop a reliable TL dating method for zircon must be most of all focused on improving the homogeneity of the sample and removing the colored, *c.q.* dark and inhomogeneous grains from the sample. This implies that extracting zircon grains from the sediment using standard mineral separation techniques such as sieving, heavy liquid and magnetic separation is not sufficient. We have developed special procedures to select homogeneous grains of the highest optical quality from the highly pure zircon fraction to improve the quality of the samples used for dating.

Another important obstacle that needs to be removed to achieve TL dating with zircon (as well as for other minerals) is (anomalous) fading of the TL signal after exposure of the samples to laboratory irradiation [1–3, 15]. Exposure to laboratory irradiation is a crucial step in the dating procedure, because it is necessary to calibrate the observed TL signal to a well-defined laboratory dose. The dating protocol is aimed at the determination of the

laboratory dose required to reproduce the natural TL signal. This dose is called the *equivalent dose (ED)*, and it is one of the most important quantities to be determined in a dating experiment. Accurate dating experiments are impossible if fading occurs after exposure of the samples to laboratory doses of ionising radiation. In some cases the problems can be overcome if sufficient efforts are made to investigate the fading processes, which should be aimed at keeping the fading effects under control.

Elsewhere [14, 16], we have developed an advanced simulation model which explains the trapping and un-trapping behaviour of electrons and holes in mineral zircon. This model also accounts for the behaviour of a variety of paramagnetic defect centres investigated with ESR [17]. During long-term natural irradiation shallow and unstable traps are emptied continuously, *i.e.* in natural samples the fading effects are included in the results and the TL signal. Of course, this process of electron/hole transfer does not occur to the same extent during short-term laboratory irradiation, because some of the defects need considerable time to reach equilibrium. Therefore, long-term natural irradiation is often imitated by a short, high dose-rate laboratory irradiation, followed by a short preheat at moderate temperatures to empty the shallow traps and bring the trapped electrons and holes to equilibrium. Although it is possible in principle to describe the trapping/un-trapping behaviour with a set of rate equations, unfortunately natural systems with numerous types of traps with a large range of trap depths are often too complex to model, which is the reason why the spontaneous emptying of shallow traps is referred to as anomalous fading. By improving the homogeneity of the sample grains, the number of traps involved in the fading processes is reduced and the problems with the modelling of the processes are reduced as well.

The TL signal of lab-irradiated mineral zircon (Fig. 1) is dominated by contributions due to recombination processes taking place at rare earth ions, which act as hole traps. During irradiation the trivalent ions, such as Dy^{3+} and Tb^{3+} , these ions are transformed into four-valent ions. This has been verified with ESR experiments on mineral single crystals from different geological localities [17]. During a few weeks' storage (in the dark) at room temperature the Dy component of the TL signal fades rapidly, implying that the radiation-induced Dy^{4+} ions are transformed into stable, trivalent Dy-ions. With ESR we have observed the radiation-induced transformation of trivalent Dy-ions to another type (probably Dy^{4+}). Unfortunately, with ESR we can detect only the trivalent Dy-ions and it does not provide information about the nature of the ions after this radiation-induced transformation. On the other hand we have concluded from recent ESR investigations, that radiation-induced transformation of trivalent rare earth ions to four-valent ones is the most probable explanation in view of our combined observations for Dy and Tb [17]. It is clear that during irradiation Tb^{3+} ions are transformed into Tb^{4+} .

In contrast with the behaviour of the Dy-TL the TL lines associated with Tb are much more stable [6]. The fadable part of the TL spectrum is removed by applying a pre-heat, prescribed by a kinetic model, which has been developed to understand the fading processes [16]. The stable component of the luminescence, in particular the strong, narrow and well-defined 545 nm Tb^{3+} peak, turned out to be suitable for dating. We note that during recombination in the TL experiment the terbium ions are transformed into the trivalent state and as a result light, which is characteristic for Tb^{3+} , is emitted. At the same time the intensity of the ESR signal of Tb^{4+} centers is reduced drastically. We have constructed several special narrow-band optical interference filters, which can be used in conjunction with our TL reader to select only the component with wavelengths of 545 nm for detection. By selecting this component of the TL signal we were able to diminish the effects of (anomalous) fading on our dating results.

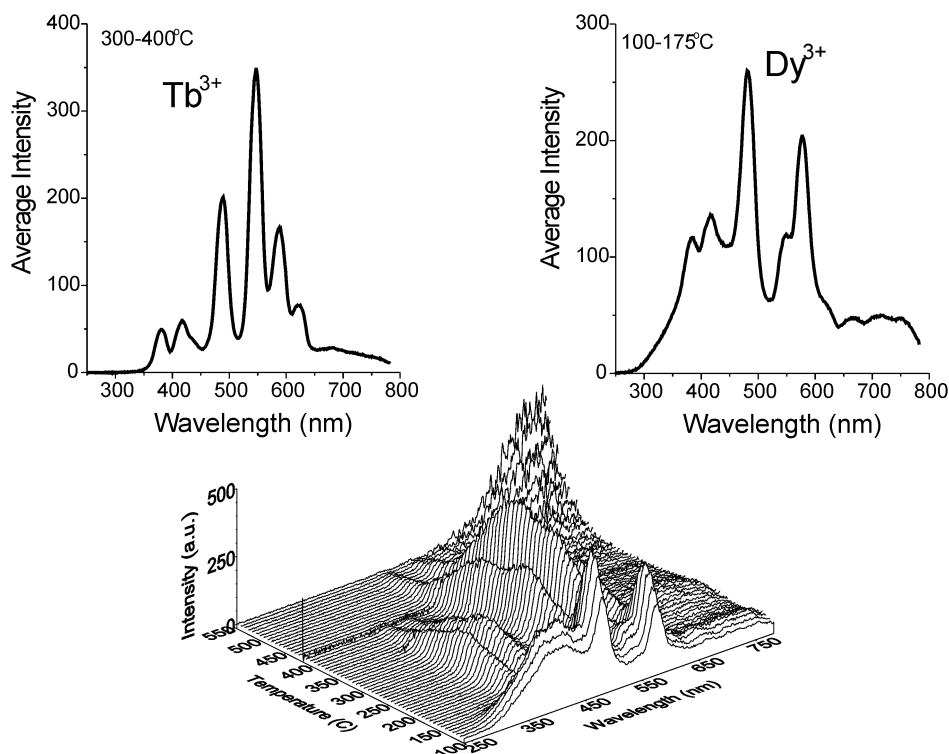


FIGURE 1 Typical 3D TL spectrum of mineral zircon, which had been irradiated in the laboratory with γ s. The two main, narrow luminescence peaks observed at low temperatures (100–175 °C) associated with the luminescence of Dy^{3+} ions, plus weaker lines due to Tb^{3+} . At high temperatures (300–400 °C) the Tb^{3+} lines dominate the emission spectrum and the contributions from Dy^{3+} are negligible.

2. THE SAMPLES AND SEPARATION/SELECTION METHODS

2.1. The Historical Zwanenwaterduinen Samples

The age-controlled samples used for this investigation were taken from the Zwanenwaterduinen region of the Dutch barrier island Ameland (Fig. 2). From historical records we know that since the 17th century Ameland was nearly split into parts several times by storm erosion. In 1686 a vessel was taken across the island, close by Zwanenwaterduinen, from the North Sea into the Wadden Sea [18] by enormous tidal waves due to a heavy storm. The dunes in this region were formed after successful efforts in the beginning of the 19th century to keep Ameland together. After a heavy storm in 1825 measures were taken including a dam, built in 1828, which resulted in sedimentation [19] and dune formation. This implies that at the time of our dating experiment in 2002 the dune sand sample was covered for about 175 years, *i.e.* optical resetting occurred about 175 years ago.

2.2. Separation and Selection of High Quality Zircon

The separation and selection procedures, used to concentrate the high quality, transparent and colourless part of the zircon fraction of the sediments are crucial elements of the zircon TL methodology. It is clear that even if a 100% pure fraction of zircon is obtained by separating

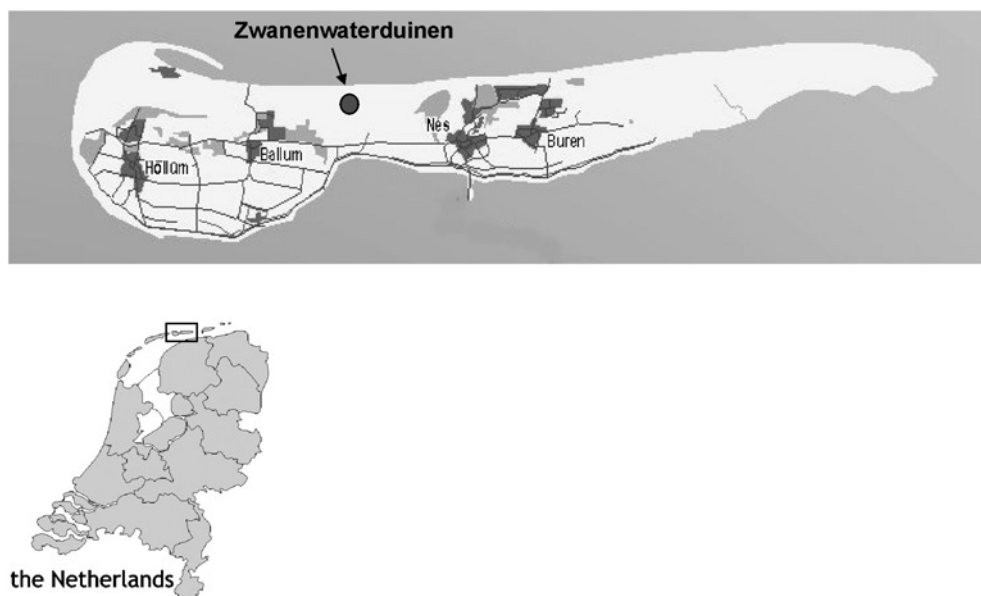


FIGURE 2 The barrier island of Ameland in the northern part of the Netherlands, showing the location of the 175-year old Zwanenwaterduinen, from which zircon sand samples were obtained for dating.

the sedimentary sample, optical inhomogeneities within the zircon concentrate might affect the TL processes. In addition, these optical inhomogeneities cause variations in the efficiency of the luminescence, because an unknown part of the TL light quanta is absorbed in the sample.

A multi-step separation/selection procedure has been designed to select the highest quality fraction of the zircon concentrate, which is used for the dating experiment. To prevent (partial) resetting of the “dating clock”, all preparations in the laboratory have been carried out in darkness or under subdued red light conditions. Typically more than 70% of the bulk sediment consists of light minerals like quartz [20], with grain sizes appreciably larger than for zircon. Through sieving, grains between 75 and 100 μm are selected and the quartz content is reduced by a factor of two. By density separation (using gravity methods, such as heavy liquid separation or separation with a shaking table), the predominant quartz sand is removed almost completely, while the percentage of zircon in the sample increases. Within the resulting fine-grained heavy mineral fraction, we have found, besides zircon, a variety of minerals such as rutile, ilmenite, magnetite and garnet. Zircon is a non-magnetic mineral. Therefore the magnetically susceptible part of the heavy fraction can be removed relatively easily by means of a magnetic separator. By increasing the magnetic field strength stepwise the ferromagnetic (*e.g.* magnetite) and the paramagnetic fraction (ilmenite and garnet) can be removed in successive separation runs. The ultimate result is an almost pure zircon concentrate (with very small amounts of quartz and rutile), in which the zircon grains vary in colour, depending on the damage level, impurity concentration, etc. Zircon used for dating should be as clear, transparent and colourless as possible. Coloured grains or grains showing light scattering by extended defects and inclusions are not suited for dating and should be excluded from the samples.

Pure zircon is an insulator. Due to long-term exposure to α -particles from U and Th nuclei, changes occur in the physical properties of insulators, including the optical absorption and the conductivity. By adding the final step consisting of a multi-stage electrostatic separation

procedure the rutile fraction can be removed successfully. In successive, iterative steps with the electrostatic separator we have also removed the coloured, heavily damaged zircon grains, which show an increased conductivity. This leaves a concentrate of homogeneous and transparent zircon grains. The efficiency of the separation process becomes obvious when observed in normal lighting. Each successive separation step leads to a product, which has a more translucent appearance. Microscopy reveals that the majority of the rejected grains are coloured zircons. After 10 stages of electrostatic separation there is no further improvement and the high-quality product represents about 10% of the initial pure zircon fraction present after the magnetic separation step.

3. TL EXPERIMENTS AND DATING RESULTS

The equivalent dose (ED) is the laboratory irradiation dose needed to reproduce the natural TL signal. The selected concentrate of dating-grade zircon was split into six equal portions of about 80 mg to allow measurements in accordance with the added-dose protocol to determine ED. Six natural TL signals were taken from samples of ~ 10 mg each from the first portion. Because these samples were not exposed to any extra laboratory irradiation source, this part of the sample had been exposed to the Natural Dose (ND) only, which is equal to the accumulated radiation dose acquired during the 175 years burial period. The remaining five portions of the sample were exposed in the laboratory to five different extra γ -doses D_i (systematic errors $\sim 3\%$) from a calibrated ^{137}Cs -source, with $D_1 = 43$ Gy, $D_2 = 88$ Gy, $D_3 = 131$ Gy, $D_4 = 175$ Gy, and $D_5 = 261$ Gy. For each dose we have carried out six TL experiments, to obtain the luminescence output as a function of the dose. ED is determined by the intersection of the straight line and the horizontal axis: $ED = 139 \pm 10$ Gy.

The 'natural TL' (NTL) of zircon grains results predominantly from internal α -irradiation of uranium and thorium impurities incorporated in the crystal lattice, while there are smaller contributions from other natural radioisotopes and cosmic rays. The activity concentrations of the relevant α -emitting nuclei in zircon have been determined with γ -ray spectrometry [21] (see Tab. I). The calculated fraction η of the α -dose deposited within the grains (of nominal diameter $90\ \mu\text{m}$) is shown in Table I. The corresponding contributions to AD given in Table I are in good agreement with the literature values [22], and we have determined the value for the total internal annual α -dose in our sample $AD_{\alpha}^{\text{internal}} = 750 \pm 30$ mGy/a. The remainder of the α -energy ($1 - \eta$) is deposited in neighbouring grains including quartz, feldspar, rutile, zircon, etc, yielding an average contribution to the annual dose in zircon grains, which is equal to $AD_{\alpha}^{\text{external}} = 4 \pm 2$ mGy/a.

Additionally, there are contributions from distant β and γ sources in the sediment, which are associated with the decay of isotopes of the U and Th series in distant grains and from ^{40}K sources in the sedimentary environment (*e.g.* feldspar). The specific activity concentrations (C) of these ^{40}K , U and Th sources for the Zwanenwaterduinen sample have been measured

TABLE 1 Activity concentrations in mineral zircon and their contributions to the Annual Dose (AD)

Isotope	Activity concentration (Bq/kg)*	Self-absorption η	Contribution of internal α -irradiation to the AD (mGy/a)
238U	3570 ± 50	0.84 ± 0.02	650 ± 30
235U	164 ± 2	0.82 ± 0.03	28.4 ± 1.4
232Th	513 ± 12	0.81 ± 0.03	76 ± 5

*Corrected for the presence of a small amount of light and heavy mineral grains other than zircon.

by gamma-ray spectroscopy and amount to $C_K = 216 \pm 3$ Bq/kg, $C_U = 58.2 \pm 0.3$ Bq/kg, and $C_{Th} = 64.0 \pm 0.7$ Bq/kg, respectively. The contribution of external β and γ radiation to the annual dose was then calculated using Monte Carlo calculations (with statistical uncertainties $<1\%$). This contribution to the annual dose is $AD_{\beta\gamma}^{\text{external}} = 30$ mGy/a.

The total annual dose is therefore $AD_{\text{total}} = AD_{\alpha}^{\text{internal}} + AD_{\alpha}^{\text{external}} + AD_{\beta\gamma}^{\text{external}} = 790 \pm 3$ mGy/a. This finding is evidence that (i) the annual dose of zircon is much higher than for quartz and feldspar and (ii) the annual dose is determined to a very large extent by the internal dose caused by α -particles. The age is given by:

$$\text{Age(years)} = \frac{\text{ED(Gy)}}{AD_{\text{total}}(\text{Gy/a})}.$$

Using the results obtained for ED and AD, we calculate that the Zwanenwaterduinen sample is 177 ± 17 years old, which is in excellent agreement with historical records of the age of formation of these dunes. This result demonstrates the utility of zircon TL as a chronometer for determining depositional age of geological deposits – even relatively young ones – and is a significant step in the development of zircon as a reliable chronometer of sedimentary events during late Quaternary time. It is significant that, with the present technology and sensitivity, samples as young as a few years may be datable, which could make zircon TL dating even a reliable tool in environmental forensic investigations.

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